Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 863

Electrohydraulic Discharge Detackifies Polymer Surfaces in Water

H. Corcoran, D.-J. Sung, and S. Banerjee

June 2000

Submitted to
Langmuir

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929 as the Institute of Paper Chemistry, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 52 North American companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide a multidisciplinary graduate education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to provide the information, expertise, and interactive learning that enables customers to improve job knowledge and business performance;
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

Electrohydraulic Discharge Detackifies Polymer Surfaces in Water

Howard Corcoran, Dong-Jin Sung, Sujit Banerjee

Institute of Paper Science and Technology
500 Tenth Street NW
Atlanta, GA 30318

Abstract

Firing a high-energy spark underwater creates a plasma channel, which partially dissipated through an acoustic field. Films of polyacrylate adhesive and wood pitch on metal coupons placed in this field are efficiently detackified. Tack reduction can also be induced through ultrasonic treatment, but at much lower efficiency. The spark-generated acoustic field generates a high concentration of hydroxyl radicals at a range of over 1.5 m. The oxygen:carbon ratio of the polyacrylate films increases upon exposure. The zeta potential of acrylate particles suspended in water and the surface pH of acrylate films both decrease upon exposure, indicating the creation of surface acidic groups.

Introduction

Polymer and other surfaces can be deactivated by corona and other gas-phase discharges (1,2). It is much more difficult to achieve a similar deactivation in water, and an efficient means of doing so would be beneficial to industries where tacky materials can disrupt operations. The recycled paper industry is one such example; adhesives introduced with the furnish can cause severe process upsets if they are not substantially removed or detackified (3,4). Recycle mills have screening and cleaning systems that remove most of the incoming adhesives. The surviving material can be bound and detackified by chemicals and minerals, but only at considerable cost. In this paper, we demonstrate that discharging a spark underwater reduces the tack of both natural and synthetic adhesives. The spark creates a plasma channel between the electrode gap (5-7). The energy released upon collapse of the channel is dissipated as heat, light, and through an acoustic field. Thus, underwater sparking can induce the same chemical reactions traditionally achieved through sonochemistry (8).

Experimental

The instrument used was obtained from Sparktec Inc., Stoney Creek, Ontario, Canada. Experiments with a submersible unit were conducted in a 130-L tank. The other assembly used was a 10-L tank constructed from a section of pipe with integrated electrodes. The 5-300 μs discharge was of 50,000 amps and 3,000-6,000 V as per manufacturer specifications. Zeta potential and particle size were measured with a Zetasizer (Malvern Instruments Ltd., UK). X-ray photoelectron spectra were taken with an incident angle of 36°.

Carbotac, an acrylate pressure-sensitive adhesive formulation, was obtained from B.F. Goodrich. Polyvinyl acetate was obtained from Air Products and Chemicals Inc. The material was coated on 316 stainless steel coupons (5.5 cm^2) and dried to a thin film. Wood pitch was obtained from Georgia-Pacific's Vienna, GA, particleboard mill as a deposit taken just after the

dryer. It was ground and heated prior to being applied to the coupon. The coupons were exposed to the sparks in water at room temperature. Unless otherwise noted, they were positioned 1.5 m and 10-15 cm from the source for work in the 130-L and 10-L tanks, respectively, with the coated surface facing the source. The electrode gaps were 3 and 5 mm for the submersible and integrated units, respectively. The spark rate ranged from 0.1 to 0.5 sparks per second. Tack was measured over a 4.5 cm^2 area with an Instron Model 4400 instrument (Instron Corp., Canton, MA) for the synthetic polymers and over a 0.2 cm^2 area with a Polyken tack tester (Testing Machines Inc., Islandia, NY) for pitch. The pitch samples were immersed in boiling water for 10 seconds, and readings were taken as the coupon cooled, with the surface temperature being monitored with a thermocouple. Ultrasonic experiments were run in 200 mL of water in an 80W Branson ultrasonic bath operating at 50 kHz. Contact angles were measured by a FTA200 Dynamic Contact Angle Analyzer (First Ten Angstroms, Portsmouth, VA).

A BioFlo 3000 reactor (a mixing tank with a Rushton impeller) from New Brunswick Scientific, Edison, NJ, was used to monitor the rate of pitch deposition (9). Pitch was ground with a mortar and pestle, homogenized, and suspended at 0.3% consistency in 500 mL of 50°C water. After 60 minutes of stirring at 300 ppm (including the initial 10 minutes of heat up), the impeller was removed, washed gently with water, oven-dried at 100°C for 15 minutes, and weighed. Replicate experiments conducted without sparking showed the uncertainty to be 4.2%.

Results and Discussion

Exposing the coated acrylate coupons to sparks increased wettability and decreased tack as shown in Table 1. The changes are insensitive to the distance of the coupon from the source and to whether the coupon faces toward or away from the spark. Hence, the reduction in tack is unlikely to be caused by the primary shock wave or the light associated with the spark. Experiments conducted with the polymer film prepared on blotting paper show similar changes in contact angle, demonstrating that a hard support is not essential for detackification.

Table 1: Tack reduction of acrylates through exposure to 5,000 V sparks

	no of sparks	**distance from source (cm)**	**contact angle (degrees)**	**tack (g/cm^2)**
130-L tank				
control	0		91	1,350
facing source	30	50	81	
away from source	30	50	76	663
close to source	30	10	78	609
close to source	60	10	83	860
10-L tank				
facing source	10	50	75	823
facing source	30	50	78	640
facing source	60	50	78	690

Table 2: Surface analysis of polymers		
		O:C ratio[1]
polyacrylate	control	0.28
polyacrylate	control	0.28
polyacrylate	40 sparks	0.32
polyacrylate	40 sparks in water containing 500 ppm NaOCl	0.30
polyvinyl acetate	control	0.35
polyvinyl acetate	40 sparks	0.42
[1]the measurement uncertainty is 0.01		

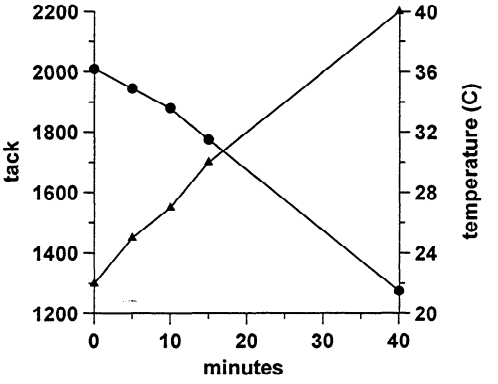

Figure 1: Effect of sonication time on tack (g/cm^2), represented by circles. The triangles represent temperature.

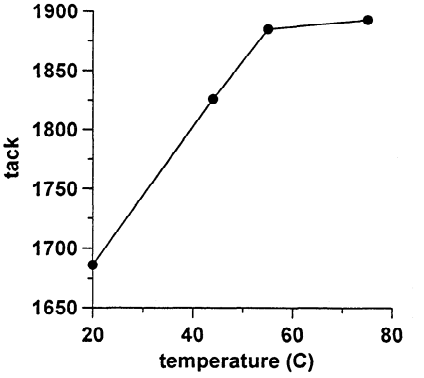

Figure 2: Effect of temperature on tack (g/cm^2).

Table 3: Hydroxyl radical oxidation of reference compounds		
	k x 10^{-9} (l $mol^{-1}s^{-1}$) measured	**k x 10^{-9} (l $mol^{-1}s^{-1}$) literature[1]**
sodium formate	4.8	3.2
thymine	2.1	6.4
sodium acetate	0.9	0.85
sodium thiocyanate	10	11
[1]from ref. 13		

The changes in surface chemistry that accompany tack reduction were measured by X ray photoelectron spectroscopy. The polymers listed in Table 2 were plated on metal coupons, and exposed to forty 5,000 V sparks; the surface O:C ratio increased in all cases, albeit by a small amount. Chlorine was detected at a level of 0.29% for the experiment run in the presence of sodium hypochlorite; no chlorine was found for the other cases. These measurements suggest a radical mechanism, with the source of oxygen being the hydroxyl radical. Oxidants can also be

generated ultrasonically in water (8, 10), and we compared the efficiency of spark-induced tack reduction to that obtained through sonication. A set of polyacrylate-coated coupons was sonicated, and coupons were removed periodically for tack measurements. The results, presented in Figure 1, show a clear decrease in tack upon sonication. The bath temperature rises during sonication, but this increases tack as illustrated by the tack-temperature relationship illustrated in Figure 2, where coupons were exposed for 10 minutes to water at different temperatures prior to the measurement.

The parallel between sonication and sparking suggests that both processes create hydroxyl radicals through cavitation, which then oxidize the polymer surface. Sparking is much more efficient. The Table 1 data show that the tack is reduced in half after exposure to 30 sparks, whereas sonication requires over 40 minutes of exposure. Although the Table 2 data demonstrates that oxidation occurs, it does not necessarily follow that oxidation is responsible for detackification; it may well be an ancillary process. Polymer chains are known to be broken through sonochemically generated shear fields (11), and it is possible that shear may contribute to detackification.

The rates of oxidation of several reference compounds by ultrasound and through exposure to sparks were measured and compared to their known oxidation rates with hydroxyl radicals. The diammonium salt of 2,2'-azinobis-(3-ethylbenzthiazoline-6-sulphonate), ABTS, is quantitatively oxidized by hydroxyl radicals with a rate constant of 1.2×10^{10} l mol^{-1} s^{-1} (12) and was used as a reference. The resulting radical cation has a characteristic absorption at 415 nm. For the ultrasonic work, the solution was monitored at 415 nm over 60 minutes. The temperature was maintained at 22°C through a heat exchanger immersed in the batch.

Oxidation rates of the compounds in Table 3 were measured by sonicating a mixture of the test compound and ABTS (1×10^{-4} M). Because some of the hydroxyl radicals were consumed by the test compound, the generation of the ABTS cation was reduced, leading to a lower absorbance. If A_o is the absorbance at 415 nm obtained by treating ABTS alone, and A is the corresponding absorbance upon sonicating the mixture, then

$$A_o/A = 1 + k_1[S]/k_2[ABTS]$$

where k_1 and k_2 are the oxidation rates of the test compound, and ABTS, respectively. The results compare well with literature values, confirming that the loss of material upon sonication is due to hydroxyl radical induced oxidation.

In order to demonstrate that hydroxyl radicals were also generated from sparking, the oxidation of 0.9 mM Fe^{2+} was monitored in the presence of various amounts of sodium acetate, whose known oxidation rate with hydroxyl radicals was used as a reference. This simpler combination was used in place of the probe compounds in Table 3 in order to avoid complications from potential photochemical reactions. Each mixture was exposed to one hundred 5,000 V sparks in a 10-L tank, and the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation was followed at 350 nm (14). A rate constant of 4.9×10^8 l $mol^{-1}s^{-1}$ was obtained for Fe^{2+} oxidation, which compares well with the reported range of $3.2\text{-}4.3 \times 10^8$ l $mol^{-1}s^{-1}$ (13) for the oxidation of Fe^2 with hydroxyl radicals.

The hydroxyl radical yield from sparking was measured by sparking 10 L of water containing 1 mM of $FeSO_4$ at a rate of 1 spark per second. Samples were drawn periodically, and the Fe^{2+} to Fe^{3+} oxidation determined. The number of hydroxyl radicals was estimated as 25% of the total number of oxidized iron atoms (15). The results are compared to hydroxyl radical generation by ultrasound and by X-rays (15) in Figure 3 and show that sparking is an efficient means of producing hydroxyl radicals. It is essential that the $FeSO_4$ be directly exposed to the sparks. No change occurs when the solution is contained in a quartz tube submerged in the tank and exposed to the sparks, confirming that it is the acoustic field and not the light that causes the oxidation.

The degree of oxidation is relatively insensitive to the applied voltage. Similar increases in absorbance were observed when a 0.1 mM $FeSO_4$ solution was exposed to sparks at charging voltages of 2,000 and 6,500 V. The range of the process is surprisingly large. Experiments with ferrous sulfate conducted in a 4,000-L tank showed that similar levels of oxidation were achieved at distances of 10 cm and 4.5 m. This is consistent with the oxidizing species being generated by the propagating acoustic wave, and not just in the plasma region.

Finally, in order to extend the work to other tacky substances, coupons coated with pitch (wood extractives) were exposed at room temperature to up to 100 sparks in the 10 L tank. Tack was measured at several temperatures since pitch is not tacky under ambient conditions. The results, illustrated in Figure 4, demonstrate a substantial reduction in tack, especially at the higher temperatures. Sparking reduces the extent of pitch deposition, as illustrated in Figure 5.

Changes in the zeta potential of acrylate and pitch particles (up to 0-100μ) induced by sparking are illustrated in Figure 6. The plot for the untreated acrylate is typical of a non-polar polymer surface. Sparking shifts the isoelectric point to lower pH, indicating the formation of acidic groups at the surface. This was confirmed by measuring surface pH of an acrylate film

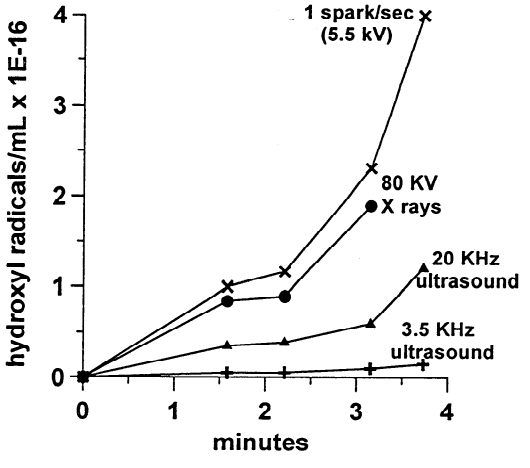

Figure 3: Comparison of hydroxyl radical formation through sparking and other means.

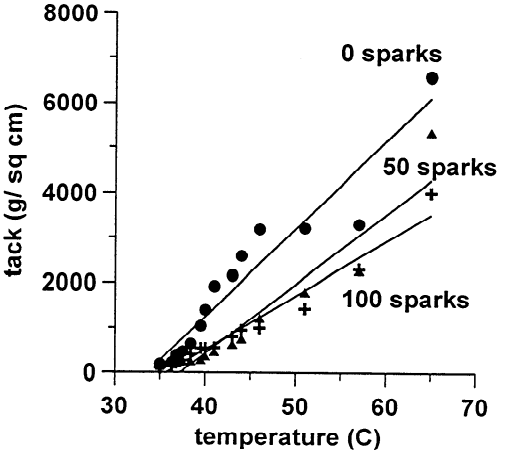

Figure 4: Effect of sparking on the tackiness of pitch.

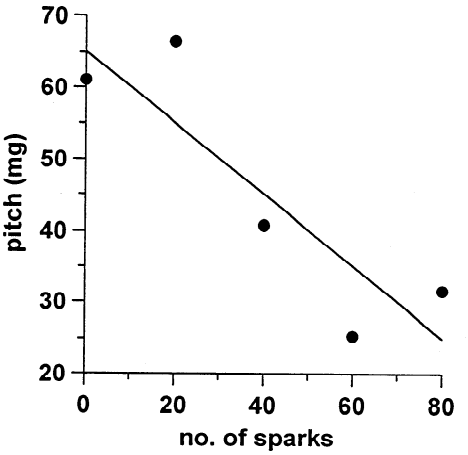

Figure 5: Effect of sparking on pitch deposition.

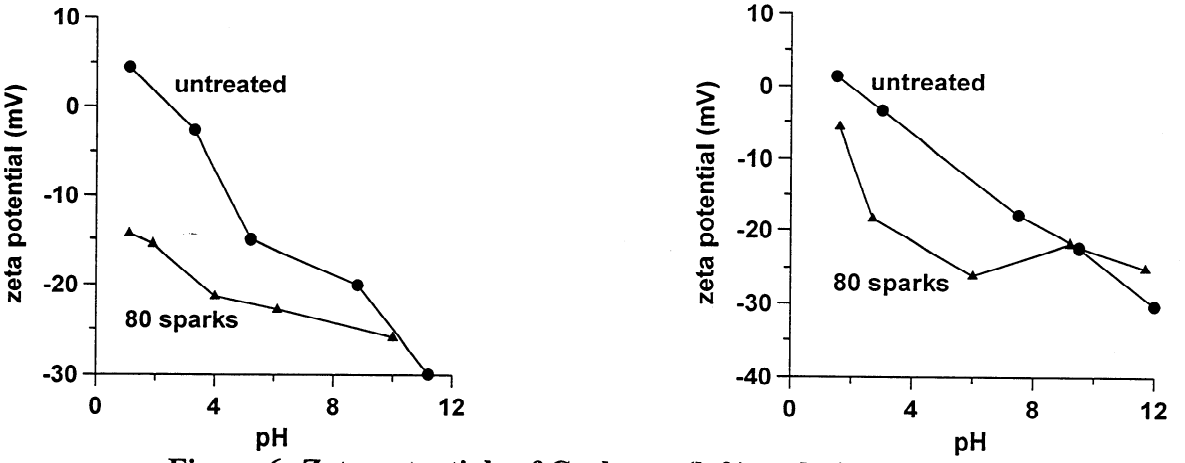

Figure 6: Zeta potentials of Carbotac (left) and pitch (right) *vs.* pH

coated on a metal coupon as a function of the number of sparks. The results, provided in Figure 7, show that sparking reduces both tack and pH. Sonication leads to similar results; treatment of a 1% suspension of Carbotac (uncured emulsion) decreased pH as shown in Figure 8.

In summary, exposure of polymer surfaces to underwater sparks leads to their oxidation, probably through hydroxyl radicals generated by the acoustic field. Although we have demonstrated that these radicals are created sonochemically, we have not unequivocally shown that they are directly responsible for reducing tack. However, the incorporation of oxygen into the surface, and the decrease in pH and contact angle make a strong case for the involvement of the hydroxyl radical. The unique attribute of the technique is that it efficiently generates hydroxyl radicals throughout a large volume, which makes it suitable for industrial applications.

Acknowledgment

This study was funded by the US Department of Energy through contract DE-FC36-99GO10381 and by the member companies of the Institute of Paper Science and Technology. We thank Dr. Lisa Detter-Hoskins at the Georgia Tech Research Institute for taking the X-ray photoelectron spectra.

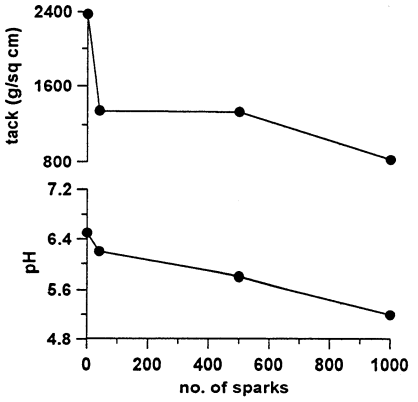

Figure 7: Tack and pH of sparked Carbotac films.

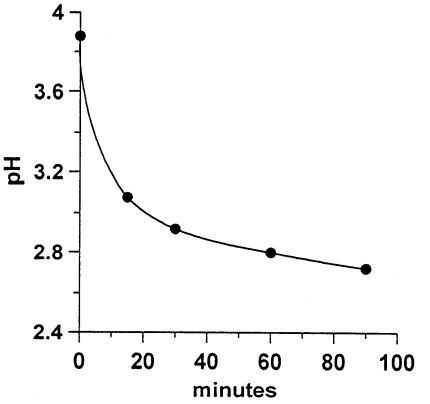

Figure 8: pH changes during sonication of a 1% Carbotac suspension.

References

1. Garbassi, F.; Morra, M.; Occhicello, E. *Polymer Surfaces. From Physics to Technology*, Wiley: Chichester, **1998**.
2. Chan, C-M. *Polymer Surface Modification and Characterization*, Hanser/Gardner: Cincinnati, **1994**.
3. Abaham, S. *Tappi J.* **1998**, *81(2)*, 79-84.
4. Ling, T. F. *Tappi J.* **1998**, *81 (3)*, 161-165.
5. Welch, C. R.; Johnson, J. W.; Blake, H.; Miller, A.; Dardeau, T.; Cooper, C.; Eng, E.; Lowry, P. Abstracts, *10th International Aquatic Nuisance Species and Zebra Mussel Conference*, Toronto, Canada, **2000**.
6. Prieto, F. E.; Loske, A. M. *Rev. Sci. Instrum.* **1991**, 62, 1849-1854.
7. Martin, E. A. *J Appl. Physics,* **1960**, 31, 255-267.
8. Mason, T. J. *Sonochemistry: The Uses of Ultrasound in Chemistry*, Royal Society of Chemistry, **1990**.
9. Farley, C. E. *Proc., TAPPI Papermakers Conference*, Chicago. **1977.**
10. Hua, I.; Hoffman, M. R. *Proc. 2nd. Int. Symp. on Environmental Applications of Advanced Oxidation Technologies*, San Francisco, **1997**.
11. Price, G. J., in Sonochemistry and Sonoluminescence, Crum, L. A., Mason, T. J., Reisse, J. L., Suslick, K. S. Eds., Kluwer Academic Publishers: Dordrecht, **1999**, pp 321-343,
12. Wolfenden, B. S.; Wilson, R. L. *J. Chem. Soc., Perkin Trans*, **1982**, 2, 805-812.
13. Buxton, G. V.; Helman, W. P.; Greenstock, C. L.; Ross, A. B. *J. Phys. Chem. Ref. Data*, **1988**, 17, 513-759.
14. Price, G; Lenz, E. *Ultrasonics* **1993**, *31*, 451-456.
15. Jana, A; Chatterjee, S. *Ultrasonics Sonochemistry* **1995**, *2* S87-9.
16. Harith, M. A.; Palleschi, A.; Salvetti, D.; Singh, D.; Vaselli, M. *J. Appl. Phys.* **1989**, *66*, 5194-5197.